

AMPHION ASSOCIATES
9 Crow Canyon Court, San Ramon, CA 94583
(415) 838-7100

US EPA RECORDS CENTER REGION 5



514303

931670

NON-RESPONSIVE

December 18, 1984

David Hird, Esq.
Environmental Enforcement Section
Land and Natural Resources Division
U. S. Department of Justice, Room 1260
10th and Pennsylvania Avenue, NW
Washington, DC 20001

Dear Mr. Hird:

Please find enclosed a draft of my first Expert Witness Report as you requested.

You will note that several items have been underlined, in addition to those underlined for emphasis. These items are those which I anticipate will be topics in my testimony and therefore need to be explicitly identified in this report.

In the event that you need to discuss any aspect of this report with me, I can be reached on Thursday morning (December 20) at (904) 376-3221 ext. 207 in Gainesville, FL. Prior to that, please contact my office in California, where Dr. John Hughes will try to assist you. In the event that you need to talk with me directly, please leave a message with him and I will attempt to call you as soon as possible from Gainesville.

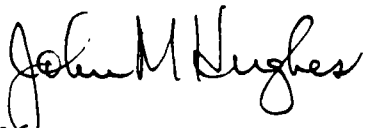
As I have already informed Paul Bitter, I will not be available between December 20 (pm) and January 2. In addition, AMPHION ASSOCIATES will be closed between Christmas and the New Year (December 24-January 1).

NON-RESPONSIVE

David Hird, Esq.
December 18, 1984
Page 2

Please be assured that we will do everything possible this week to provide you with an appropriate Expert Witness Report prior to closing for the holidays.

Yours sincerely,


for B. J. Kimble, Ph.D.

BJK/JMH: pc

Enclosure

cc: Bill Sierks, DOJ
Paul Bitter, EPA

This document is being sent by electronic mail (Federal Express ZapMail) with the original following by overnight delivery.

AMPHION ASSOCIATES
9 Crow Canyon Court, San Ramon, CA 94583
(415) 838-7100

NON-RESPONSIVE

December 18, 1984

David Hird, Esq.
Environmental Enforcement Section
Land and Natural Resources Division
U.S. Department of Justice, Room 1260
10th and Pennsylvania Avenue, NW
Washington, DC 20001

Dear Mr. Hird:

As you know, Dr. Kimble has conveyed to me by telephone the revisions to her expert witness report in order that you can receive it before the holidays. However, neither of us have been able to reach Paul Bitter on either Monday or Tuesday of this week to obtain the necessary guidance on the following matters relating to documents supplied to Dr. Kimble:

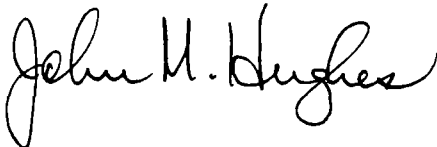
1. Whether reference 5 in the enclosed report (a USGS internal document) should be included in Dr. Kimble's testimony.
2. The exact form of citation for the Minnesota Department of Health data (reference 3) which is primarily a collection of memos and data sheets, rather than a more conventional report or publication.

Accordingly, we have included both citations in this version of the report. When Mr. Bitter receives his copy and/or can be reached, these matters will be resolved and we can provide you with a final version that incorporates those decisions.

David Hird, Esq.
December 18, 1984
Page 2

Again, please be assured that we are doing everything possible to provide you with an appropriate Expert Witness Report before AMPHION ASSOCIATES closes for the holiday period. If you have any questions regarding the enclosures, please contact me at this office.

Very truly yours,



John M. Hughes, Ph. D.

JMH: pc

Enclosures (2)

cc: Bill Sierks, DOJ
Paul Bitter, EPA

This document is being sent by electronic mail (Federal Express ZapMail) with the original following by overnight delivery.

AMPHION ASSOCIATES

9 Crow Canyon Court, San Ramon, CA 94583
(415) 838-7100

NON-RESPONSIVE

December 18, 1984

EXPERT WITNESS REPORT

This report has been prepared by Dr. Brenda J. Kimble of AMPHION ASSOCIATES, California, at the request of David Hird, Esq. of the U.S. Department of Justice, and in connection with current litigation relating to the former Reilly Tar & Chemical Corporation site in St. Louis Park, Minnesota.

Introduction.

The Reilly Tar & Chemical Corporation operated a coal tar distillation and wood preserving plant in St. Louis Park, Minnesota for over five decades up to 1972. The materials used in these processes (the original starting materials, the distillation products, and the products from the wood preserving process) are composed of a vast array of chemicals of which most are organic in nature.

Among these many chemicals, however, a significant number belonged to a class of chemicals known as Polycyclic Aromatic Hydrocarbons or "PAH", which are compounds containing carbon and hydrogen atoms in various configurations of rings. Other compounds include phenolic compounds whose structures contain groups with an oxygen atom joined to a hydrogen atom (an "OH" or "phenolic" group), and compounds related to the PAH but which also contain one or more nitroge

EXPERT WITNESS REPORT

December 18, 1984

Page 2

In order to understand the fate of these chemicals, both at present and in the future, several reports^{1,2,3,4,5,6} have been reviewed in terms of their analytical and environmental chemistry perspectives.

Analytical Chemistry.

In order to determine the types and amounts of chemicals that may be present in environmental samples, portions of the sample, whether water, soil, air particles, etc., have to be analyzed for their constituent chemicals which may be either organic (i.e., containing carbon, such as in biological tissues), or inorganic (such as common salt), or both.

¹"Results of Analysis of Water Samples, Sludge Sample and Soil Samples for Polycyclic Aromatic Compounds (Hydrocarbons, Azaarenes, Phenols)", by E. E. Conrad, J. R. Guthrie and E. M. Hansen, Midwest Research Institute, Kansas City, MO 64110; Final Report, EPA Contract NO. 68-02-2814, Assignment No. 21, MRI Project No. 4468-L(21), October 7, 1981.

²"Evaluation of Groundwater Treatment and Water Supply Alternatives for St. Louis Park, Minnesota, by CH2M Hill and Barr Engineering Co.; prepared for Minnesota Pollution Control Agency, November 1983.

³Data generated by the Minnesota Department of Health laboratories.

⁴"Degradation of Phenolic Contaminants in Ground Water by Anaerobic Bacteria: St. Louis Park, Minnesota", by G.G. Erlich, D. F. Goerlitz, E. M. Godsy and M.F. Hult, Ground Water 20, 703 (1982).

⁵"Preliminary Evaluation of Ground-Water Contamination by Coal-Tar Derivatives, St. Louis Park Area, Minnesota", M.F. Hult and M. E. Schoenberg, U.S. Geological Survey Water-Supply Paper 2211, prepared in cooperation with the Minnesota Department of Health, 1984.

⁶Data generated for the Reilly Tar & Chemical Corporation by Monsanto Research Corporation under contract to Environmental Research and Technology, Inc.

EXPERT WITNESS REPORT

December 18, 1984

Page 3

In the case of the products that were used at the Reilly Tar facility, the majority were organic in nature and were derived from natural starting materials by thermal processes such as distillation. As these starting materials were themselves a complex array of organic compounds, and they were then subjected to thermal processes (which generally tend to increase the total number of chemicals in materials), the resulting suite of chemicals associated with activities at the Reilly Tar site would be unusually complicated in terms of the number of possible organic species.

In order to analyze such environmental samples for their chemical constituents, an appropriate analytical method has to be chosen which will ensure that, with a specified degree of certainty, the final results do in fact represent the true nature and concentration of those identified chemicals as they occurred in the environment. Once a method is selected, a protocol is developed that defines in detail the exact procedures that will be used both for sample collection "in the field" and for sample analysis in the laboratory. This protocol would include the procedures for sample preparation prior to analysis, such as the extraction of organic compounds out of water or soils.

In carrying out such procedures, a variety of controls are included in the protocol so that the analyst and others can be sure that the procedures are working as expected and that the protocol is being followed closely. Such controls normally include the use of "standards" (authentic, highly characterized, pure samples of the specific chemical compounds), which are also used to determine the sensitivity of the particular analytical method, that is, the limit of detection for the given chemical. This latter parameter -- usually called the detection limit -- is the concentration in the environmental matrix below which the analytical method cannot detect the compound of interest, and so the analyst cannot be sure whether or not the chemical is present or not below that limit.

EXPERT WITNESS REPORT

December 18, 1984

Page 4

After identification of the compounds present in the sample, a quantitation procedure (also described in the protocol) is carried out to determine the concentration of that chemical in the sample.

Analytical Methods.

As mentioned above, the majority of chemicals associated with the Reilly Tar facility are organic compounds which are present in a complex mixture. In the analysis of such complex mixtures in environmental samples, the organic compounds are first separated from the water or soil or other matrix, to give a complex extract for identification and quantitation.

Chromatography: Because of the complexity of these types of samples, the mixture must then be separated into its component chemicals prior to the identification and quantitation process. In modern laboratories, this is normally carried out by a technique known as column chromatography, which involves the partitioning of a compound between two materials called phases which are contained in a chromatographic column. One of the phases is mobile and moves continuously from one end of the column to the other; the other is fixed inside the column and is therefore known as the stationary phase.

Since the relative affinities of compounds for the two phases, and hence their partitioning, is determined by their chemical structure, the chromatographic process results in the separated components leaving the end of the column at different times based on the percentage of time they spent in the mobile phase compared to the stationary phase, and this percentage is determined by their chemical structures. Thus, for a given set of chromatographic conditions, each chemical has a characteristic time associated with it, known as the retention time, which is measured from the start of the analysis when the unseparated mixture was introduced into the inlet of the chromatographic instrument. If a suitable detector is used at the end of the column, a tracing (a chromatogram) can be produced which allows

EXPERT WITNESS REPORT

December 18, 1984

Page 5

the analyst to measure the elution of the components of the mixture as a series of "peaks" with corresponding retention times and areas. By comparison of these retention times and areas with those of standards which have been analyzed in separate experiments but under the same conditions, a tentative identification can be made as well as a determination of the corresponding concentration.

High Pressure/Performance Liquid Chromatography (HPLC): One type of chromatography which is frequently used for the analysis of organic compounds (particularly those that are present in water samples, and often for compounds such as PAHs), is High Pressure Liquid Chromatography (HPLC), also known as High Performance Liquid Chromatography (see EPA Method 610⁷ for the analysis of PAHs). This technique uses a liquid (which may be organic or aqueous or a mixture of both) as the mobile phase, and the liquid chromatograph can be fitted with a detector that is very sensitive for PAH and related compounds (more sensitive than most GC/MS analyses, see below). At the current state-of-the-art used by most commercial laboratories, however, the degree of resolution or separation of the components of a mixture is not as great as can be achieved by gas chromatography (see below).

Gas Chromatography (GC): This more common type of chromatography utilizes a gas as the mobile phase and can be carried out with either a column that is packed with the stationary phase (see EPA Method 610⁷ for the analysis of PAHs), or a column in which the column has a very narrow bore (a "capillary") and is coated on the inside with the stationary phase. Unlike HPLC, both types of gas chromatography can only be used for compounds whose structures are sufficiently small and non-polar that they can be chromatographed as a vapor within the gaseous mobile phase. Further, the use of

⁷Polynuclear Aromatic Hydrocarbons-- Method 610, in EPA-600/4-82-057, July 1982, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater.

EXPERT WITNESS REPORT

December 18, 1984

Page 6

capillary columns provides a significant increase in the ability of the GC column to separate compounds having similar retention times, as compared to packed columns.

Gas Chromatography/Mass Spectrometry (GC/MS): One potential limitation of the chromatographic methods described above is that compound identification is only achieved by comparison of the retention time with that of standards. This means that, while a given compound has a unique retention time under a given set of chromatographic conditions, more than one compound can have the same retention time. Further, in the analysis of the unknown components of a complex organic mixture, this factor affects the confidence with which the reported identification can be made. It is certain, however, that if a peak with a given retention time is absent in a chromatogram, then the corresponding standard compound is not present at levels above the detection limit of the method.

In order to increase the confidence of such identifications, a more complex type of detector (known as a mass spectrometer and abbreviated as "MS") is used at the end of the chromatographic column to form an instrument known as a combined gas chromatograph/mass spectrometer, abbreviated as GC/MS (see EPA Methods 624³ and 625⁴). At the current level of common use, a mass spectrometer is used only as a detector for GC columns and not for HPLC columns due to various engineering considerations, but either packed or capillary GC columns can be accommodated.

The mass spectrometer detector is operated in such a way as to continuously and repetitively record a

³Purgeables-- Method 624, in EPA-600/4-82-057, July 1982, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater.

⁴Base Neutrals, Acids, and Pesticides-- Method 625, in EPA-600/4-82-057, July 1982, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater.

EXPERT WITNESS REPORT

December 18, 1984

Page 7

"structural fingerprint" (the mass spectrum) of whatever compounds may be eluting out of the end of the GC column. For identification purposes, both the mass spectrum and the retention time must match the standard compound, as recorded in separate experiments. As the mass spectrum is a highly complex piece of structural information containing many facets (such as a fingerprint), the correspondence of both the retention time and the mass spectrum provides a high degree of confidence in the resulting identification. In addition, the high information content of the mass spectrum allows a qualified analyst to determine the purity of the eluting peak and hence to make an assessment of the accuracy of the quantitative measurement (the concentration) which is derived from the total area for the peak on the chromatogram.

In practice, the matching of the mass spectra and retention times can be carried out either by computer techniques (a procedure known as "library-matching" in which the data for the standards are stored in a library in the computer), or by "manual" methods by a experienced mass spectrometrists. Although the latter method can and often does incorporate the same library-matching computer techniques, the analyst also uses the rules that have been generated over the approximately forty years of mass spectrometry to interpret the mass spectral fingerprint in terms of the chemical structure of the compound. This extra interpretive stage also serves to increase the confidence in the final analytical result: the concentrations of the chemicals in the sample under study.

"Chemical Fingerprinting".

Following chemical analysis of the environmental samples, the concentration data from different samples can be examined in an attempt to understand chemically what is happening in the environment from which the samples were derived. For example, a chemical explanation can be made for the migration of chemicals in groundwater by comparing the identities and

EXPERT WITNESS REPORT

December 18, 1984

Page 8

concentrations of chemicals in a series of water samples taken from wells in the area under study.

In the case of groundwater contamination from a localized source such a manufacturing facility or a leaking hazardous waste dump site, analysis of water from wells remote from the source and up-gradient of the source would show no detectable pollutant chemicals, or, if the concentrations exceeded the detection limit of the analytical method used, the analyses would show "background levels" (from natural or man-made sources) that were common to that broad geographical area.

In general, samples taken from wells at or near the source would be expected to contain the highest concentrations of the pollutant chemicals provided that the pollution incident was of a sufficient magnitude to still be a source of chemicals to the groundwater.

Further, if analyses of water samples from wells in the vicinity of the source showed concentrations (at levels above background) of some or all of the pollutant chemicals that were identified at the source, then the chemical interpretation would be that those pollutants had migrated in the groundwater from the source to this site. For this interpretation to be chemically consistent, it is not a requirement for all of the source pollutants to be found at this site, since not all organic chemicals are water-soluble. Like the chromatographic process outlined above, organic chemicals will only move in the mobile phase (the water), and not in the stationary phase (the soil or other geological matrix), and so the "plume" of chemicals emanating from the source will, in general, parallel the partitioning of chemicals between the mobile and stationary phases, leading to the most water-soluble chemicals at the front edge of the plume, and the least water-soluble trailing far behind or even still at the source.